

PATENT SPECIFICATION



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(54) POLYMERISATION PROCESS

(71) We, ROHM G.M.B.H. (formerly known as Rohm & Haas G.m.b.H.), a German Body Corporate, of Darmstadt, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Water-soluble polymers such as for example the alkali metal salts of polyacrylic or polymethacrylic acid, polyacrylamide or polyvinylpyrrolidine, are commonly used as flocculation agents, sedimentation and filtration aids or as thickening agents for aqueous solutions, such polymers being more effective for these purposes the higher molecular weight. Polymers with molecular weights of several millions may be obtained by polymerisation of water-soluble monomers in concentrated aqueous solution with efficient cooling of the polymerisation heat whereby extremely highly viscous to rigid gel solutions are obtained. Among the methods for producing such polymers on an industrial scale reversed pearl polymerisation is advantageous in certain cases in view of the simplicity of the apparatus used and the ease of regulation. In this process the aqueous monomer solution containing a polymerisation initiator is suspended in an organic liquid immiscible with water and the system is kept at the polymerisation temperature.

In practice however many difficulties occur in performing this process. For example as polymerisation progresses the droplets of aqueous monomer solution pass through a stage of pronounced tackiness when they tend to agglomerate and to be deposited on the stirrer and vessel walls. In certain cases it has been possible to overcome this tackiness by the use of dispersing agents, such as hydrophobic kaolins and bentonites, silanised silicic acid and other fine-particle solids as well as soluble additives such as cellulose esterified with polar fatty acids, polymers of hydrophobic monomers with hydrophilic substituents or low molecular

surface active agents. However, these agents have hitherto only had a limited success since for example they have proved to be inadequate with reversed pearl-polymerisation of acrylates or methacrylates containing a quaternary ammonium group on the alkyl radical.

We have now found that the suspension polymerisation of ethylenically unsaturated monomers can be effected advantageously in an organic liquid medium by using certain macromolecular compounds (as hereinafter referred to) as suspension stabilisers.

According to one feature of the present invention we provide a process for the polymerisation of a monomer composition comprising at least one ethylenically unsaturated monomer, which process comprises polymerising the monomer composition in the liquid phase, the said liquid phase being suspended in a liquid organic medium and the polymerisation being effected in the presence of a macromolecular compound, at least one polymeric portion of which is solvatable by the liquid monomer phase while at least one other polymeric portion of which is solvatable by the liquid organic medium, the said macromolecular compound serving to stabilise the suspension.

The suspension polymerisation process according to the invention differs from conventional pearl-polymerisation processes in that a continuous organic phase is used instead of the continuous aqueous phase. The process according to the invention also differs from the known reversed pearl-polymerisation process in the type of emulsifier used.

The liquid monomer phase can in the most simple case consist of a liquid monomer or monomer mixture which is either not or only soluble to a limited extent in the organic medium e.g. vinylimidazole, N-vinyl pyrrolidone. It is simply sufficient for the monomer phase to be liquid under the polymerisation conditions in the process according to the in-

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vention. Thus for example acrylamide which melts at 85° C can be polymerised above its melting point or in a mixture with a liquid monomer such as vinyl pyrrolidone, below its melting point as a suspended liquid phase in a liquid medium consisting of hydrocarbons.

Preferably, however, the monomers are polymerised according to the process of the invention in the form of solutions whereby the solvent for the monomers and the organic medium are selected such that they are either not miscible or only miscible to a limited extent. Aliphatic or aromatic hydrocarbons such as petroleum distillate or xylene as well as chloro-hydrocarbons such as tetrachloroethylene, may advantageously be used as the organic polymerisation medium.

Preferred organic solvents for the monomer phase include for example glycols such as ethylene glycol, propylene glycol, butane-diol, di- and tri-methylene glycol as well as glycerin, formamide, formic acid and acetonitrile, provided that the monomers to be polymerised and the resulting polymer dissolve therein but not in the hydrocarbons employed as the organic polymerisation medium. Even when these precautions are taken it is desirable to ensure that the total combination does not form a homogeneous phase via dissolving intermediaries. A polymerisation initiator is generally employed in the process and should preferably be soluble in the monomer phase but not in the organic medium. Undesired precipitation polymerisation in the liquid organic medium can generally be avoided if the monomers or the initiators only dissolve in trace amounts in the liquid medium e.g. a limited solubility of the initiator or the monomer alone in the organic medium is not harmful.

The use of the reactants in the opposite sense is also possible, i.e. the glycols, formamides, acetonitrile or succinic acid form the continuous liquid medium and the polymer is produced from a solution of the monomers in a hydrocarbon or chlorohydrocarbon solvent. The monomer phase preferably consists of an aqueous solution of a monomer and the organic medium comprises a liquid immiscible with water such as aromatic or aliphatic hydrocarbons, chlorohydrocarbons, esters, higher alcohols or higher ketones. In systems of this type water-soluble monomers which may be employed include for example salts, preferably the alkali metal salts, of acrylic acid, methacrylic acid, maleic acid, fumaric acid or itaconic acid; acrylamide or methacrylamide, N-vinyl pyrrolidone, vinyl-pyridine, vinyl-imidazole, dialkylamino-alkyl esters or amides of acrylic or methacrylic acid e.g. dimethyl-aminoethyl methacrylate, β -morpholinoethyl acrylate or diethylamino methylmethacrylamide, particularly the salts of such amino group-containing monomers with organic or inorganic acids such as acetic acid, p-toluene sulphonic acid or hydrochloric acid as well as the

quaternisation products which can be prepared from the amino group-containing monomers by reaction with alkyl halides in particular methyl chloride or with dimethyl sulphate or similar alkylating agents.

The above-described process according to the present invention is particularly suitable for the preparation of water-soluble pearl polymers from monomer compositions comprising quaternary or acid addition salts of dialkylaminoalkyl esters or amides of acrylic or methacrylic acid and, if desired, one or more additional water-soluble monomers such as salts of acrylic, methacrylic, maleic, fumaric or itaconic acid, acrylamide or methacrylamide, N-vinylpyrrolidone, vinylpyridine, or vinyl-imidazole. Such pearl polymers are novel compounds and constitute a further feature of the present invention. These pearl polymers advantageously comprise 20 to 100% by weight of salts and/or quaternisation products of dialkylaminoalkyl esters or amides of acrylic or methacrylic acid, e.g. trimethyl- β -methacryloxyethyl-ammonium chloride or methosulphate. The new polymers may, if desired, contain 20 to 80% by weight of acrylamide and/or methacrylamide and/or up to 50% by weight of sodium methacrylate.

The concentration of the monomers in the particular solvent used generally depends on their solubility and one generally employs a monomer concentration suitable for the polymer solution to be prepared, and at the end of the polymerisation the polymer solution is separated from the organic medium. If a solvent-free polymer in the form of solid pearls is to be produced from a monomer which is not liquid at polymerisation temperature then one preferably uses for the monomer a solvent which boils at a considerably lower temperature than the organic medium or which forms an azeotropic mixture therewith, the solvent being conveniently separated by distillation at the end of polymerisation. For example, suspended aqueous polymer can be easily and completely dehydrated by azeotropic distillation with aliphatic hydrocarbons, aromatics or chlorohydrocarbons. If desired, however, the liquid medium may only partly comprise a liquid boiling azeotropically with the solvent of the monomer phase. For example, the liquid medium can consist of a mixture of a paraffin oil and a chlorohydrocarbon which has the advantage that during dehydration non-inflammable vapours are formed as a result of azeotropic distillation. A complete separation of the solvent is in many cases unnecessary in order to isolate non-tacky pearls. In such cases, it is generally unnecessary to remove the final amounts of the solvent which can possibly amount to 30% by weight in the polymer, but if desired, removal of the solvent can be effected in a drying oven, rotary dryer or the like.

Preferred polymerisation initiators are those

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- which are conventionally used in solution or bulk polymerisation of the particular monomers concerned, provided that they are substantially insoluble in the organic medium.
- 5 Thus for example for the polymerisation of a suspended aqueous monomer solution alkali metal or ammonium persulphates, 4,4'-azobis-4-cyanopentanoic acid or water-soluble redox systems are preferably used. When the monomers are completely insoluble in the organic phase, one can, if desired, use initiators of the azo-bis-isobutyronitrile type which are distributed between both phases of the polymerisation system. The initiators are generally used in the quantities and at the temperatures which are also conventional in pearl, solution or bulk polymerisation.
- The dispersion of the monomer phase comprising more or less spherical particles may be advantageously effected according to the invention by ensuring a turbulent movement of the reaction mixture.
- 20 The quantity and effectiveness of the stabilizing agent must be greater the more pronounced the tendency of the disperse phase to coalesce to form a continuous phase or to agglomerate into large aggregates. In addition to the desirability of maintaining a turbulent movement for the mixture, the viscosity of the disperse phase and the density difference between the two phases are also important. Suitable conditions are known from conventional pearl polymerisation and are generally applicable to the process according to the invention. The lower the turbulence of the reaction mixture and the higher the viscosity of the monomer phase at the time of adding the stabilizing agent and the lower the quantity of the stabilizing agent, the larger the particles formed by the monomer phase. Thus for example the particle size can be increased either by adding the stabilizing agent only at a time after the start of polymerisation by which the viscosity of the monomer phase has already increased as a result of polymer formation, or by adding a thickening agent which can be dissolved in the monomer phase. A stabilizing agent is considered to be well suited for the proposed purpose if the suspended monomer phase required at least 15 minutes to be deposited in a layer. The quantity of the stabilizing agent can be kept particularly low if the density of the organic medium is largely matched to the density of the monomer phase. This can be achieved in a simple manner by mixing two organic liquids, one of which has a lower density, while the other a higher density than the monomer phase. For aqueous monomer phases organic media comprising a hydrocarbon e.g. petroleum distillate, paraffin oil or toluene and a chlorohydrocarbon e.g. trichlorethylene or tetrachlorethane, are for example particularly advantageous.
- 65 The stabilising agents used in the proce-

according to the invention are analogous in structure to low molecular surface-active agents i.e. they may be, e.g. block or graft copolymers with polymeric portions of varying solvophilicity, at least one polymeric portion of which is solvatable by the organic medium while at least one polymeric portion is solvatable by the monomer phase so that the stabilisers collect at the boundary surface between both phases. This tendency is particularly marked if the stabilising agent is only limitedly soluble in both phases. Good solubility of the stabilising agent in one or both phases reduces the portion of the polymer molecules located at the phase boundary surface. The solubility behaviour is essentially determined by the relative proportions of polymeric portions of varying solvophilicity. If the solvophobic portion is smaller than the solvophilic portion then the tendency of the stabiliser to collect at the boundary surface is reduced and the emulsifying action drops. Preferably therefore the ratio of the aggregate molecular weight of the portion(s) of the copolymer solvatable by the liquid monomer phase to the aggregate molecular weight of the portion(s) of the copolymer solvatable by the organic medium is in the range of 10:1 to 1:10, particularly advantageously between 2:1 and 1:2.

The selection of suitable monomers for composing the various polymeric portions of the stabilisers in general depends only on the solvophilicity of the monomers relative to the particular phase. Thus, water-soluble monomers yield hydrophilic polymeric portions. Water-soluble monomers can be classified as neutral, anionic or cationic. Neutral water-soluble monomers are e.g. acrylamide and methacrylamide or vinylpyrrolidone. The hydrophilic molecular portions of the stabiliser may also comprise polyvinyl alcohol or polymers with units of the vinyl alcohol as well as polymers of ethylene and propylene oxide. Anionic monomers include for example water-soluble salts of copolymerisable carboxylic acids or sulphonic acids, particularly alkali metal salts as well as the corresponding free acids such as e.g. acrylic and methacrylic acid, fumaric, maleic or itaconic acid, methacryltaurin, vinyl sulphonic acid or m-styrene sulphonic acid. Preferred cationic monomers include for example vinylpyridine, vinylimidazole, vinylimidazoline and homologues of these compounds, aminoalkyl esters of acrylic acids or methacrylic acid particularly those with tertiary amino groups such as dimethylaminoethyl methacrylate and the water-soluble salts and quaternary ammonium compounds thereof. Polymers of ethylene diamine can also form the hydrophilic portion of the stabilizers.

Monomers which form water-insoluble homopolymers can, if desired, be incorporated to a limited extent in the composition of the hydrophilic polymer chain segments or graft

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5	branches, examples of such monomers including the monoesters of acrylic or methacrylic acid with ethylene glycol, propylene glycol, 1,4-butane-diol or glycerine or more or less hydrophobic monomers such as alkyl acrylates or methacrylates, styrene and vinyl esters. Such monomers should be used in smaller quantities the more hydrophobic they are themselves and the less hydrophilic the other co-monomers are. Thus, for example a copolymer of 70 parts methylacrylate and 30 parts sodium acrylate is still water-soluble. However, when using methacrylamide as a hydrophilic monomer a hydrophilic molecule portion must not contain more than 20% by weight of water-insoluble monomers.	Thus the solution of a cationic monomer can be polymerised in the presence of a stabilizer with an anionic, cationic or non-ionic hydrophilic polymeric portion. The same applies for anionic monomers.
10	Surprisingly the ionogenity of a monomer to be polymerised in a suspended aqueous solution need not be taken into consideration when selecting the hydrophilic molecule portion.	For liquid phases of the polymerisation system with less hydrophilic and more hydrophobic character, stabilizing agent, components with an accurately adapted solvophilicity can be produced by the correct selection of starting materials. The following table gives groups of suitable solvophilic molecular portions for a number of classes of non-aqueous liquid phases (designated A, B . . . etc) whereby there is a certain interchangeability within each class although generally the tendency towards more hydrophobic components increases generally from top to bottom in each class.
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40	<i>Liquid Phase</i>	<i>Solvophilic Molecular Portion</i>
45	A) Lower Alcohols (C_1-C_4) Formamide Acetonitrile	Polymer chains of: Acrylic or methacrylic acid Fumaric, maleic, itaconic acid Methacrylaurin Vinylsulfonic acid m-Styrene sulfonic acid Vinylpyrrolidone Vinylimidazoline Vinylimidazole Vinylpyridine N-Vinylpyridone Dimethylaminoethyl methacrylate
50	B) Glycerine Ethylene glycol Propylene glycol 1,4-butanediol	Vinyl alcohol Ethylene oxide Propylene oxide
55	C) Higher alkanols (C_6-C_{12}) Cyclohexanol	Hydroxyethylacrylate or methacrylate Hydroxypropylacrylate or methacrylate Butanediol-monoacrylate or methacrylate Hexanediol-monoacrylate or methacrylate
60	D) Chloroform Carbon tetrachloride Trichlorethylene Tetrachlorethylene Tetrachlorethane Ethyl acetate Butyl acetate Methyl propionate Acetone Methylethylketone Methylisobutylether	Methyl acrylate Ethyl acrylate Butyl acrylate Butyl methacrylate Isobutyl acrylate or methacrylate Vinyl acetate Vinyl propionate Vinyl butyrate Styrene
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<i>Liquid Phase—continued</i>		<i>Solvophilic Molecular Portion—continued</i>
		Polymer chains of:
F)	Benzene Toluene Xylene Decalin Aliphatic hydrocarbons Petroleum ether Paraffin oil	Styrene Vinyltoluene α -Methylstyrene Hexyl acrylate or methacrylate 2-Ethyl-hexyl-acrylate or methacrylate Decyl, dodecyl, octadecyl-acrylate or methacrylate, fumarate, maleate Vinyloctoate Vinylesters of "Versatic acids" (the word "Versatic" is a registered Trade Mark) Vinylstearate
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As regards the liquid phases or solvophilic molecular portions not mentioned in this list 15 of examples the conventional rule that like dissolves like can in general largely be followed. However, the polar character of the monomer phase is not only influenced by the solvent used but with an increasing monomer or monomer mixture content also by the polar character thereof. The more strongly the monomer or monomer mixture determines the polar character of the monomer phase the more the corresponding polymer can be considered as 20 a suitable solvophile for the monomer phase. However exceptions to this rule occur where as for example with acrylonitrile the polymer is insoluble in the monomer. The monomer phases consisting completely or mainly of 25 monomers are arranged in the above table according to their polar character. For connecting the molecular portions of varying solvophilicity or their monomer precursors to dispersion-effective block or graft copolymers it 30 is possible to proceed in a variety of ways. Examples of convenient processes for the preparation of graft polymers are described hereinafter:

1. By irradiating a base polymer or by 35 the action of radicals formed from polymerisation initiators one can obtain radical points on the base polymer from which graft branches are formed in the presence of graft monomers. In addition to the graft polymer a large 40 quantity of the non-grafted polymer of the graft monomer(s) is often formed. The latter polymer has no dispersing action and when used dissolves as a stabilizer in the phase for which it has the larger solvophilicity. Due to 45 this undesired side-effect the use of stabilizers produced by static grafting is not generally preferred for preparing the stabilisers used in the invention.

2. A considerably larger amount of grafted 50 polymer is obtained if the graft monomer is polymerised in the presence of a base polymer which contains unsaturated side groups. The preparation of such polymers is generally known and usually takes place by reacting 55 a polymer containing reactive groups with a compound having a complementary reactive

group and a radically polymerisable double bond. Suitable reactive groups include for example anhydride, carboxylic chloride, carboxy, epoxy, isocyanate or azlactone groups on the one hand and hydroxyamino or hydrazino groups on the other. For example copolymers with units of maleic anhydride, itaconic anhydride, acrylic or methacrylic chloride, glycidyl acrylate or methacrylate, vinylisocyanate or 2-isopropenyl-4,4-dimethyl-oxazolone-5 can be reacted with allyl alcohol, hydroxyalkyl esters of acrylic or methacrylic acid, acrylic or methacrylic acid ethanolamide, methylol-acrylamide, methylol-methacrylamide, aminoalkyl esters of acrylic or methacrylic acid or acrylic or methacrylic hydrazide. If the polymer contains units of acrylic, methacrylic, maleic, fumaric or itaconic acid then the above-mentioned reactions can also be effected under sufficiently rigorous reaction conditions. The reverse case whereby the said monomers are incorporated in a polymer and are reacted with the free monomers which serve as a basis for the above mentioned polymer components is also possible for the preparation of polymers with unsaturated side-groups. Finally such polymers can alternatively be prepared in one stage if monomers with two unsaturated double bonds of varying reactivity are subjected to co-polymerisation under conditions where only one double bond is predominantly polymerised. Preferred monomers of this type are e.g. allyl acrylate and methacrylate. 65

By radical polymerisation of the graft monomer in the presence of the polymer with unsaturated side-groups a graft polymer-like product can be obtained. The polymerisation graft branches can be regulated in such a way, e.g. with the addition of transfer regulators that the resulting polymer approximately corresponds to the quotient of the number of equivalents of unsaturated monomers and the number of equivalents of unsaturated side-groups of the total base polymer. With a higher polymerisation level cross-linking occurs whilst lower polymerisation levels lead to the formation of polymers of the graft monomers not connected to the base polymer. 70

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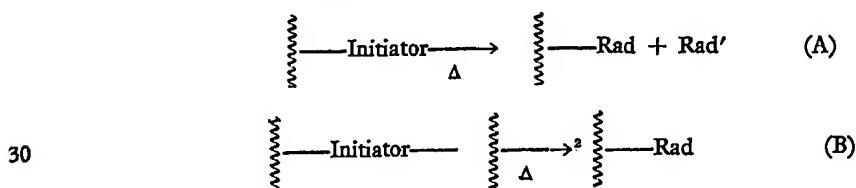
3. The condensation or addition reactions described under 2 can be used, if desired, to connect together complete molecular portions of varying solvophilicity. In this process one can prepare independently two polymers of varying solvophilicity with reactive groups complementary to one another and react said polymers. To prevent cross-linking at least one of the polymers should contain not more than an average of 1 reactive group per macromolecule.

4. Advantageously the graft polymers are produced from those base polymers which carry side-fixed azo or peroxy groups, the

formation of graft branches being initiated by the radical decomposition of the said groups, in the presence of graft monomers. A distinction can be made between the cases namely.

- A) the azo or peroxy groups are connected on one side with the macromolecule (Diagram A, wherein initiator is understood to mean a grouping having an azo or peroxy group and optionally containing further groups) and

B) the azo or peroxy groups are connected on both sides with a chain of the macromolecule (Diagram B)



In case C as a result of the decomposition of one initiator group two radical points (Rad) linked to macromolecules are formed which represent the starting point of a graft branch.

35 However, in Case A in addition to the radical (Rad) linked to the macromolecule a free radical (Rad') is formed from which a non-grafted polymer chain results. If this non-grafted portion is disadvantageous an initiator-
 40 containing basic polymer of type B is preferably used.

The preparation of the initiator-containing base polymer should be carried out under conditions where the azo or peroxy groups do not decompose. It is produced from an unsaturated radically polymerisable monomer with an azo or peroxy group by radical copolymerisation then an initiator having a much lower decomposition temperature should be used. Preferred polymerisable initiators as well as the conditions under which they can be polymerised without decomposing are described for example in German Patent 1,055,240. With particular advantage the polymerisable derivatives of azo-bis-isobutyric monoamide, diamide, monohydrazide or dihydrazide, are used since these compounds have decomposition temperatures above 100°C and can be copolymerised below this temperature with conventional polymerisation initiators. Such compounds include for example

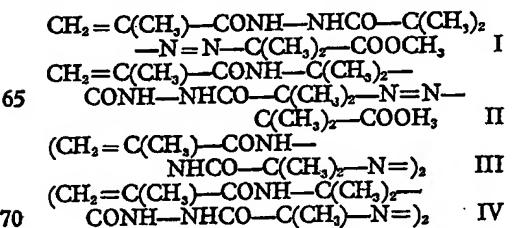
wherein the carbon double bond-containing molecular portion in the case of compounds I and III is for example derived from methacrylic chloride and in the case of compounds II and IV from 2-isopropenyl-4,4-dimethyl-oxazolone-5. The azo group containing molecular portion in the case of compounds I and II is derived for example from azo-bis-isobutyric monohydrazide monomethyl-ester and in compounds III and IV from azo-bis-isobutyric dihydrazide.

A base polymer with units of monomers of formulae I to IV can also be obtained from copolymers of acrylic or methacrylic chloride or 2-isopropenyl-4,4-dimethyloxazolone-5 and reaction of the polymer with one of said azobis-isobutyric hydrazides. This mode of preparation of the base polymer can be used, in principle with other azo or peroxy group-containing compounds or with different reactive groups in the base polymer e.g. methacrylic or maleic anhydride groups.

Preferred block polymers for use as stabilisers in the process according to the invention may be obtained for example by the following processes:—

- processes.

 1. As a result of shearing forces (mastification) on a polymer in the presence of a monomer of a different solvophilicity radical points are formed as a result of chain breakage at which block polymers of the added monomer can be formed.
 2. Two polymers of different solvophilicity can be masticated together, and by radical chain breaking of a polymer molecule and recombination with fractions of the other polymer, block polymers can be formed.
 3. Two polymers of different solvophilicity with complementary reactive terminal groups can be reacted together to produce block polymers. For example, one of the polymers



- can be prepared in the presence of mercaptoacetic acid as the regulator or 4,4'-azo-bis-4-cyanopentanoic acid as the initiator and the other in the presence of mercaptoethanol. On heating, preferably in the presence of an acid catalyst, the carboxyl groups of the one react with the hydroxyl groups of the other polymer with the formation of ester groups.
4. A water-insoluble monomer is suspended in droplet form in the aqueous solution of a monomer which contains an initiator which is only soluble in water e.g. potassium persulphate. During the polymerisation of the water-soluble monomer in the aqueous phase the growing chain end can penetrate the phase boundary surface of the droplets of suspended monomer and extend further therein with the formation of a block of suspended polymerised monomer. The homopolymers of both monomer types are generally formed as by-products but these do not generally detrimentally effect the emulsifying action of a block polymer; however if desired they can easily be separated by selective extraction.
- 25 The quantity of block or graft polymer used as the stabilising agent is generally from 0.01 to 10% by weight based on the monomer or monomer mixture to be polymerized, preferably from 0.1 to 2% by weight.
- 30 The process according to the invention is advantageously carried out in such a way that the stabilising agent is introduced into the liquid organic medium and the monomer phase to which a polymerisation initiator has already been added is allowed to flow in accompanied by vigorous stirring. The monomer phase is thereby divided into approximately spherical droplets generally of 0.1 to 3 mm diameter. The sequence in which the components are added is however not critical and can differ from the manner described here. The temperature of the reaction mixture is preferably kept approximately constant during polymerisation. Generally a cooling jacket through which water flows is sufficient to carry off the heat of polymerisation but in larger reaction vessels a cooler coil can be incorporated or the use of a cooled stirrer can be advantageous. The polymerisation time depends on many factors and in a typical case can amount to 2 to 4 hours after an approximately 1-hour induction period. The reaction product can for example be precipitated in the form of solid polymer pearls by introducing a solvent-free monomer phase. These can also be obtained by distilling off or removing in some other way the solvent if a monomer phase containing water or another solvent is used for the polymerisation. The polymer pearls can be filtered off or be converted into a solution by adding a suitable solvent.
- Although the process of the invention is particularly advantageous for the production of water-soluble polymerisation products such as flocculation agents, sedimentation aids, dye-
- ing aids, antistatic finishing aids, thickening agents, hair fixing agents, water-soluble binders and the like fundamentally a wide variety of other polymerisation products can be likewise prepared. It is thus possible to produce according to this process e.g. molding substances for the production of molded article, fibres or films, process aids for molding substances, coating and binding agents, adhesives, viscosity index improving agents for lubricants, textile aids such as finishing and sizing agents.
- The following Examples are given by way of illustration only; in the examples parts refer to parts by weight.
- Preparation of suspension stabilizers*
- A) In a solution of 25 parts of trimethyl- β -methacryloxyethylammonium - chloride, 2 parts of a copolymer prepared from equal portions of dimethylaminoethylmethacrylate and butyl methacrylate as well as 0.2 parts of 4,4' - azo - bis - 4 - cyanopentanoic acid in 75 parts of water are suspended in 25 parts of butyl methacrylate with vigorous stirring. Under a carbon dioxide atmosphere the mixture is heated for 3 hours at 70°C and, after adding a further 0.14 parts of the initiator, for 1 hour at 75°C. A viscous white dispersion with a 40% polymer content is obtained. The resulting polymer at 20°C in a 1% solution in an ethyl-glycol-dioxane mixture (96.5:3.5 parts) has an $\eta_{sp}/c = 0.6$.
- B) 29.1 parts of butyl methacrylate, 0.9 parts of azo - bis - N - [methacrylamidoisobutyryl] - isobutyric - hydrazide (prepared from 2 mol of 2 - isopropenyl - 4,4' - dimethyl oxazolone - 5 and 1 mol of azo - bis-isobutyric hydrazide) and 0.3 parts of ethyl azo - bis - isobutyrate are dissolved in 70 parts of ethylene glycol and heated for 4 hours under a carbon dioxide atmosphere at 80°C. Then a solution of 20 parts of trimethyl - β - methacryloxyethylammonium chloride in 47 parts of ethylene glycol are added followed by heating for 4 hours at 115°C. A whitish cloudy solution with a 30% dry content and a viscosity of 1500 cP is obtained.
- C) The process described under B) is repeated except that instead of butyl methacrylate a mixture of this ester with β -hydroxypropyl acrylate (weight ratio 23.1:6) is used. The solution obtained has a viscosity of 1750 cP.
- D) The process described under B) is repeated except that instead of the solution of trimethyl - β - methacryloxyethylammonium-chloride a solution of 12.9 parts of acrylamide in 30 parts of ethylene glycol is used. A 30% solution with a viscosity of 1500 cP is obtained.
- E) The process described under B) is repeated except that instead of trimethyl - β -methacryloxyethylammonium - chloride the same amount of methacrylic acid is used. The

- 30% solution obtained has a viscosity of 1200 cP.
- F) 36 parts of decylmethacrylate, 4 parts of isopropenyl - 4,4 - dimethyl - 5 - oxazolone-5 and 0.5 parts of t - butyl - peroctoate are dissolved in 60 parts of white spirit and the solution is heated to 80° C for 4 hours under a carbon dioxide atmosphere. The polymer solution obtained is mixed with a solution of
- 10 84 parts of ethyl acrylate, 9.5 parts of 2-hydroxypropylacrylate and 2 parts of azo-bis-isobutyric hydrazide and a mixture of 120 parts of benzene solution and 20 parts of glacial acetic acid. On heating the reaction mixture the azo-bis-isobutyric hydrazide is added to the 4,4 - dimethyl - 5 - oxazolone-5 groups of the polymer formed in the first stage. By heating for 4 hours at 115° C a 39% cloudy whitish solution with a viscosity of 19—cP is obtained. For the graft polymer $\eta_{sp}/c = 0.05$ was determined at 20° C in chloroform.

Preparation of suspension polymers

In all tests the subsequently described procedure was followed:

The organic phase and the dissolved distributing agent are placed in a vessel with stirrer. After expulsion of the air by means of inert gas the solution is heated to 70° C and the initiator-containing monomer phase is added accompanied by vigorous stirring (300 rpm). Polymerisation usually commences after between one half and one and one hours and is completed after three hours.

If the monomer phase contains water this is removed azeotropically at the end of polymerisation until hard non-tacky pearls are obtained. In tests 5 and 6 the solvent-free polymer is obtained directly. In tests 7 and 8 the polymer pearls obtained are freed of solvent by washing with acetone.

The details of the tests are given in the following tables.

Composition of the Phases

Test No.	Monomer Phase (mixing ratio in parts by weight)	Liquid Organic Medium (mixing ratio in parts by weight)
1	Acrylamide, TMAC ¹⁾ (80 : 20) 60% in water	Tetrachlorethylene and n-hexane (66 : 34)
2	Trimethyl-β-methacryloyloxyethylammonium-methosulfate, 70% in water	Tetrachlorethylene + benzine 2) (52 : 48)
3	Trimethyl-β-methacryloyloxyethylammonium-methosulfate, acrylamide (80 : 20), 60% in water	ditto
4	Methacrylic acid, urea (50 : 50) 67% in water	Xylene
5	2-Hydroxyethylacrylate, acrylamide (50 : 50), solvent-free	Petroleum distillate 2)
6	N-vinylimidazole, acrylamide (50 : 50), solvent-free	Petroleum distillate 2)
7	Methacrylic acid, 60% in formamide	Tetrachlorethylene, n-hexane (67 : 33)
8	Methacrylic acid, methacrylonitrile (70 : 30),	ditto

Composition of the Phases (continued)

Test No.	Monomer Phase (mixing ratio in parts by weight)	Liquid Organic Medium (mixing ratio in parts by weight)
9—10	TMAC, 75% in water	Benzene
11	ditto	Toluene
12	TMAC, acrylamide (20 : 80) 75% in water	Benzene
13—14	TMAC, acrylamide (80 : 20) 75% in water	ditto
15	TMAC, dimethylaminoethyl-methacrylate-hydrochloride (20 : 80), 75% in water	ditto
16	TMAC, acrylamide, meth-acrylamide (20 : 40 : 40), 70% in water	Benzene
17	TMAC, sodium-methacrylate (50 : 50), 50% in water	ditto
18	Acrylamide, sodium-meth-acrylate (70 : 30), 53.5% in water	ditto
19	Sodium-methacrylate, 40% in water	ditto
20	Sodium-acrylate, 36% in water	ditto
21	Na-acrylate, Na-methacrylate (47 : 53) 44% in water	ditto
22	Na-acrylate, Na-methacrylate (80 : 20) 40% in water	ditto
23	TMAC, Sodium-methacrylate (50 : 50), 70% in water	ditto

1) TMAC, = Trimethyl-β-methacryloxyethyl-ammonium-chloride

2) Boiling range 80—110°C

Polymerisation Conditions

Test No.	Phase ratio of liquid medium to monomer phase (parts by volume)	Suspension stabilizer		Initiator		Regulator Quantity ⁴⁾ 1)	Viscosity of 1% aqueous solution of the polymer in cP, 20°C.
		Quantity 1)	Type 2)	Quantity 1)	Type 3)		
1	2.5 : 1	0.5	A	0.03	ACP	0.005	2000
2	2.5 : 1	0.5	A	0.02	ACP	—	2500
3	2.5 : 1	0.5	A	0.02	ACP	0.005	1500
4	2.5 : 1	5.0	A	0.05	ACP	—	45
5	7 : 1	5.0	F	0.05	ACP	0.5	4
6	7 : 1	5.0	F	0.05	ACP	0.1	400
7	2.5 : 1	1.0	A	0.05	ACP	—	500 5)
8	2.5 : 1	1.5	A	0.25	ABE	—	—
9	9 : 1	20	B	0.5	APS	—	500
10	4 : 1	10	C	0.01	APS	—	400
11	2 : 1	2	A	0.01	APS	—	2200
12	3 : 1	10	C	0.025	NPy	—	600
13	2 : 1	2	A	0.01	APS	—	5400
14	2 : 1	2	E	0.01	APS	—	600
15	2 : 1	2	A	0.01	APS	—	2200
16	2 : 1	2	A	0.01	APS	—	1500
17	2.5 : 1	2	A	0.02	APS	—	400
18	2.5 : 1	5	A	0.05	APS	—	1000
19	2.5 : 1	3	A	0.05	APS	—	80
20	2.5 : 1	3	A	0.05	APS	—	15000
21	2.5 : 1	5	A	0.05	APS	—	2400
22	2.5 : 1	2	E	0.03	APS	—	8200
23	2.5 : 1	2	E	0.02	APS	—	500

1) Quantity in parts by weight based on the monomer weight

2) Compare preparation processes A to F

3) ACP = 4,4'-azo-bis-4-cyanopentanoic acid, ABE = azo-bis-isobutyric acid ethylester,
APS = ammonium persulfate, NPy = sodium pyrosulfite, polymerisation at 30°C.

4) Mercaptoethanol

5) Measured as sodium salt

WHAT WE CLAIM IS:—

1. A process for the polymerisation of a monomer composition comprising at least one ethylenically unsaturated monomer, which process comprises polymerising the monomer composition in the liquid phase, the said liquid phase being suspended in a liquid organic medium and the polymerisation being effected in the presence of a macromolecular compound, at least one polymeric portion of which is solvatable by the liquid monomer phase while at least one other polymeric portion of which is solvatable by the liquid organic medium, the said macromolecular compound serving to stabilise the suspension. 70
2. A process as claimed in claim 1 in which the liquid organic medium comprises an aliphatic or aromatic hydrocarbon and/or an aliphatic chlorohydrocarbon. 75
3. A process as claimed in claim 2 in which the liquid organic medium comprises a mixture of an aliphatic hydrocarbon and per-chlorethylene. 80
4. A process as claimed in any of the preceding claims wherein the said liquid organic medium and the liquid monomer phase are of approximately the same density. 85
5. A process as claimed in claim 1 wherein the monomer composition is substantially insoluble in the liquid organic medium at the polymerisation temperature and is present in the form of a solution thereof in a solvent which is substantially insoluble in, or immiscible with the said liquid organic medium at the polymerisation temperature. 90
6. A process as claimed in claim 5 wherein the solvent in which the monomer composition is dissolved comprises ethylene glycol, propylene glycol, butane-diol, di- or tri-methylene glycol, glycerine, formamide, formic acid or acetonitrile. 95
7. A process as claimed in claim 5 wherein the solvent in which the monomer composition is dissolved comprises water. 100
8. A process as claimed in claim 1 or claim 7 wherein the monomer composition comprises a water-soluble salt of acrylic acid, methacrylic acid or maleic acid; acrylamide or methacrylamide; N-vinyl-pyrrolidone, vinyl-pyridine or vinyl-imidazole; or a dialkylamino-alkyl ester or amide of acrylic or methacrylic acid or a water-soluble acid addition or quaternary salt of such an ester or amide. 105
9. A process as claimed in claim 8 wherein the monomer composition comprises an alkali metal salt of acrylic or methacrylic acid. 110
10. A process as claimed in claim 8 wherein the monomer composition comprises dimethyl-aminoethyl methacrylate, β -morpholinoethyl acrylate or diethylaminomethyl methacrylamide. 115
11. A process as claimed in claim 8 wherein the monomer composition comprises trimethyl- β -methacryloxyethylammonium chloride. 120
12. A process as claimed in any of the preceding claims wherein the macromolecular compound comprises a graft or block copolymer, at least one polymeric portion of which is solvatable by the liquid organic medium while at least one other polymeric portion is solvatable by the liquid monomer phase. 125
13. A process as claimed in claim 12 wherein the ratio of the aggregate molecular weight of the portion(s) of the copolymer solvatable by the liquid monomer phase to the aggregate molecular weight of the portion(s) of the copolymer solvatable by the organic medium is in the range of 10:1 to 1:10. 130
14. A process as claimed in claim 12 wherein the ratio of the aggregate molecular weight of the portion(s) of the copolymer solvatable by the liquid monomer phase to the aggregate molecular weight of the portion(s) of the copolymer solvatable by the organic medium is in the range of 2:1 to 1:2.
15. A process as claimed in any of claims 12 to 14 wherein the macromolecular compound comprises a graft copolymer wherein either the base chain thereof is solvatable by the organic medium and the grafted chain thereof is solvatable by the liquid monomer phase or the base chain thereof is solvatable by the liquid monomer phase and the grafted chain is solvatable by the liquid organic medium.
16. A process as claimed in claim 1 wherein the liquid organic medium comprises a C₁—C₄ alcohol, formamide or acetonitrile and the macromolecular compound comprises at least one polymeric portion solvatable with the organic medium and containing units derived from acrylic or methacrylic acid; fumaric, maleic or itaconic acid; methacryltaurin, vinylsulphonic acid, m-styrene-sulphonic acid, vinyl-pyrrolidone, vinyl-imidazoline, vinyl-imidazole, vinyl-pyridine, N-vinyl-pyridone or dimethylaminoethyl methacrylate.
17. A process as claimed in claim 1 wherein the liquid organic medium comprises glycerine, ethylene glycol, propylene glycol or 1,4-butane-diol and the macromolecular compound comprises at least one polymeric portion solvatable with the organic medium and containing units derived from vinyl alcohol, ethylene oxide or propylene oxide.
18. A process as claimed in claim 1 wherein the liquid organic medium comprises an alcohol containing 6 to 12 carbon atoms or cyclohexanol and the macromolecular compound comprises at least one polymeric portion solvatable with the organic medium and containing units derived from hydroxyethyl acrylate or methacrylate, hydroxypropyl acrylate or methacrylate, butane-diol monoacrylate or monomethacrylate or hexane-diol monoacrylate or monomethacrylate.
19. A process as claimed in claim 1 wherein the liquid organic medium comprises chloroform, carbon tetrachloride trichloroethylene, tetrachloroethylene, tetrachloroethane, ethyl

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- acetate, butyl acetate, methyl propionate, acetone, methylethylketone or methylisobutyl ether and the macromolecular compound comprises at least one polymeric portion solvatable with the organic medium and containing units derived from methyl acrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate or methacrylate, vinyl acetate, vinyl propionate, vinyl butyrate or styrene.
- 10 20. A process as claimed in claim 1 wherein the liquid organic medium comprises benzene, toluene, xylene, decalin, an aliphatic hydrocarbon, petroleum ether or paraffin oil and the macromolecular compound comprises at least one polymeric portion solvatable with the organic medium and containing units derived from styrene, vinyl-toluene, α -methyl-styrene, hexyl acrylate, or methacrylate, 2-ethyl-hexyl acrylate or methacrylate, decyl, dodecyl or octadecyl acrylate, methacrylate, fumarate or maleate, vinyl octoate or vinyl stearate.
- 15 21. A process as claimed in any of the preceding claims wherein the said macromolecular compound is employed in an amount of 0.01 to 10% by weight of the said monomer composition.
- 20 22. A process as claimed in claim 21 wherein the said macromolecular compound is employed in any amount of 0.1 to 2% by weight of the said monomer composition.
- 25 23. A process as claimed in any of the preceding claims wherein the said macromolecular compound is introduced into the liquid organic medium in which the monomer composition is suspended, prior to polymerisation.
- 30 24. A process as claimed in claim 1 substantially as herein described.
- 35 25. A process for the polymerisation of ethylenically unsaturated monomers substantially as herein described in any of the Examples.
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26. Polymers whenever prepared by a process as claimed in any of the preceding claims.
27. Water-soluble pearl polymers prepared by the polymerisation of monomer compositions comprising quaternary or acid addition salts of dialkylaminoalkyl esters or amides of acrylic or methacrylic acid.
- 45 28. Water-soluble pearl polymers as claimed in claim 27 wherein the monomer composition contains additional water-soluble monomers.
29. Water-soluble pearl polymers as claimed in claim 28 wherein the said further water-soluble monomer comprises salts of acrylic, methacrylic, maleic, fumaric or itaconic acid, acrylamide or methacrylamide, N-vinylpyrrolidone, vinylpyridine or vinylimidazole.
- 50 30. Water-soluble pearl polymers as claimed in any of claims 27 to 29 containing 20 to 100% by weight of salts and/or quaternisation products of dialkylaminoalkyl esters or amides of acrylic or methacrylic acid.
31. Water-soluble pearl polymers as claimed in any of claims 27 to 29 containing 20 to 80% by weight of acrylamide or and methacrylamide.
- 55 32. Water-soluble pearl polymers as claimed in any of claims 27 to 29 containing 20 to 100% by weight of trimethyl- β -methacryloxyethyl-ammonium-chloride or methosulfate.
33. Water-soluble pearl polymers as claimed in any of claims 27 to 29 containing up to 50% by weight of sodium methacrylate.
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